

SYNTHETIC CLAY-SUPPORTED CATALYSTS FOR COAL LIQUEFACTION

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ABSTRACT

Synthetic clays with nickel substitution in the lattice structure are highly active catalysts for hydrogenation and hydroisomerization and, consequently, have considerable promise for the catalytic upgrading of coal liquids. Nickel-substituted synthetic mica montmorillonite (NiSMM) was prepared and subsequently impregnated with molybdenum and sulfided. The reaction of model compounds with these catalysts in the presence of hydrogen has been investigated to provide mechanistic models for coal liquefaction. The results indicate that NiSMM has active Brönsted acid sites for hydrocracking and hydroisomerization. The hydrogen-activating ability of the molybdenum and nickel sulfide sites proximate to the acid sites results in effective depolymerization catalysis.

INTRODUCTION

Acid smectite clays have been used as catalysts in petroleum-cracking and various other reactions. Unfortunately, they dehydrate and collapse at temperatures above 200°C. In pillared clays, intercalation of hydroxylated or complexed metal cations maintains the clay layer structure after loss of water and generates large micropore volumes. These structures are stable to 450° and 500°C. The alumina cluster-pillared clays are effective supports for use in hydrogenation and hydrocracking catalysis as well as in coal liquefaction (1-3). Chromia-pillared clays with even larger pore spacings have considerable potential for upgrading large coal macromolecules (4). Schobert and others reported copper-impregnated montmorillonite was effective for catalysis of coal liquefaction (5).

Synthetic clays were reported to be more active catalysts than natural clays (6-8). Synthetic mica montmorillonite (SMM) containing cobalt or nickel or another hydrogen-activating component dramatically improves the hydrocracking and hydroisomerization activity (9-12). Exactly how the activity is enhanced is not known (13). In the EERC catalyst program, a selection of synthetic clays with and without incorporated hydrogen-activating components were tested for coal liquefaction as well as with model compounds. The catalysis of C-S and alkyl-aryl bond breakage as well as arene hydrogenation and hydroisomerization of n-alkanes was investigated.

EXPERIMENTAL

Catalyst Preparation. NiSMM was prepared by the procedure of Heinerman and others (14). SMM was prepared by the procedure from the French patent (15).

Preparation of Clay-Supported Molybdenum Catalysts. The synthetic clays were loaded with 5 wt% molybdenum using the incipient wetness method. Ammonium molybdate tetrahydrate (0.046 g) was dissolved in 50 mL of deionized water. To this solution 0.5 g of desired clay was added and stirred overnight. The solvent was removed by evaporation, and the resulting product was calcined in air at 350°C for 6 hours.

Sulfidation. The catalyst was placed in a 12-mL microreactor. The reactor was evacuated and pressurized with 200 psi of hydrogen sulfide. The reactor was placed in a rocking heater preheated to 350°C. The heating was continued for 3 hours. The reactor was cooled to room temperature, degassed, and opened. The catalyst was recovered and stored in airtight bottles.

Reduction. Nickel-substituted synthetic mica montmorillonite was reduced in hydrogen (1000 psi) at 450°C for 16 hours. The reduction was carried out in a microreactor heated in a rocking heater as described above.

Catalytic Reactions. In a typical run, 0.5 g of model compound and 0.25 g of the catalyst were placed in a tubing bomb (12-mL microreactor). The microreactor was evacuated, pressurized with 1000 psig of hydrogen, and placed in a rocking autoclave heated to desired temperature. The heating was continued for 3 hours. At the end of the reaction period, the microreactor was cooled in a dry ice-acetone slurry, degassed, and opened. The desired amount of the internal standard was added to the product slurry, and the product slurry was transferred into a centrifugation tube by washing with methylene chloride and the solid catalyst removed by centrifugation. The liquid sample was analyzed by gas chromatography(GC)/flame ionization detection(FID) and GC/Fourier transformation infrared (FT-IR)/mass spectroscopy (MS). The solid was dried in vacuum at 110°C for 3 hours.

RESULTS AND DISCUSSION

Synthetic mica montmorillonite (SMM) and nickel-substituted synthetic mica montmorillonite (NiSMM) were prepared and used as supports for molybdenum sulfide. Both the synthetic clays and the molybdenum-loaded catalysts were tested for hydrocracking, hydrosulfurization, hydroisomerization, and hydrogenation activities using bibenzyl, pyrene, dibenzothiophene, and *p*-cresol as test substrates.

Bibenzyl Cracking. The synthetic clay support materials were tested to determine their reactivities prior to molybdenum incorporation. The reaction of bibenzyl with synthetic mica montmorillonite (SMM) gave a very small conversion of bibenzyl into products. However, in the nickel-substituted SMM, where octahedrally coordinated aluminum ions were replaced by nickel ions, the hydrocracking activity increased considerably. The reaction of bibenzyl with NiSMM catalyst converted 67% of bibenzyl into lighter products. Major products were benzene and ethylbenzene. Formation of these products is indicative of a carbonium ion mechanism catalyzed by Brönsted acid sites (16). This mechanism proceeds via ipso protonation followed by cleavage of the aryl-alkyl bond to form the phenylethyl carbonium ion intermediate. The carbonium ion is then reduced to the alkyl group. Ethylbenzene is further cracked to benzene via the same steps, the extent depending on the activity of the catalyst. The formation of toluene may have been Lewis-acid catalyzed. In addition to these products, a very large number of other products in much smaller concentrations were also observed. Detailed characterization of these products is under investigation. These products may have been formed from the hydrogenation, hydroisomerization, or ring-opening reactions. No oligomeric material was observed.

NiSMM was reported to have activity comparable to that of zeolites. It was suggested that nickel-substituted clays crystallize in smaller platelets, resulting in more exposed edges and, consequently, higher surface area and increased activity (13). Based on the FT-IR measurements of adsorbed ammonia on NiSMM, it has been shown that the number of Brönsted acid sites increases following Ni reduction (14, 17). These newly created acidic sites are responsible for the increased activity of NiSMM compared with SMM in which no nickel is substituted for Al^{3+} in the octahedral sites. Robschlager and others (17) reported that for this catalyst to be active for the isomerization of pentane, lattice Ni^{2+} has to be reduced to zero-valent nickel, and the activity of the catalyst decreased when metallic nickel was removed by treatment with carbon monoxide. In contrast, the bibenzyl hydrocracking data for the reduced NiSMM indicates that the activity of the catalyst did not change significantly with reduction of Ni^{2+} to metallic nickel. In fact, a slight decrease in the catalytic activity was seen for the reduced catalyst. However, reduction of the Ni^{2+} during hydrotreating cannot be ruled out.

Sulfidation of the NiSMM gave a substantial increase in catalytic activity for hydrocracking. The reaction of bibenzyl with presulfided NiSMM gave significantly higher conversion (82%) than NiSMM. The product distribution was similar to that of NiSMM reaction. Small amounts of benzene and alkylbenzenes were converted into cyclohexane and cycloalkanes probably by NiS-catalyzed hydrogenation of the single aromatic rings. The increase in hydrocracking activity on sulfidation might be attributed to a facilitation of the addition of hydrogen to some intermediate involved in hydrogen (hydride) transfer, but further work is required to fully understand the nature of the catalytic activity in the NiSMM catalysts.

The reaction of bibenzyl with SMM- and NiSMM-supported MoS_2 gave significantly higher conversions (34% and 92%, respectively) of bibenzyl into products. Major products were found to be benzene, toluene, and ethylbenzene. Small amounts of cyclohexane, methyl cyclohexane, and ethyl cyclohexane were also formed. A significant portion of the bibenzyl was reduced to benzylcyclohexane and other hydrogenated products, but no oligomeric products were formed. Extensive conversion to isomeric aliphatic compounds also occurred. The conclusion from the hydrocracking experiments is that the NiSMM is a very active support for the molybdenum sulfide and the combination has high activity as a hydrogenation, hydrocracking, and hydroisomerization catalyst.

Almost quantitative amounts of catalyst were recovered at the end of each reaction. Unlike highly acidic zeolite catalysts, these catalysts do not catalyze retrogressive reactions or coke formation (18).

Hydrogenation of Pyrene. Pyrene was used as a test compound to investigate hydrogenation activity of NiSMM catalysts. The reactions were carried out by heating pyrene and the desired catalyst at 350°C for 3 hours in the presence of 1000 psi of molecular hydrogen. The effects of sulfiding the NiSMM and supporting the (MoS_2) hydrogenation catalyst on NiSMM were also investigated.

The reaction of pyrene with NiSMM gave a high conversion (90%) of pyrene into hydrogenated products. The majority of the products were di-, hexa-, and decahydropyrenes. Small amounts of hexadecahydro- and tetrahydropyrenes were also

formed. Numerous other components were formed by hydrocracking and rearrangement reactions.

The synthetic clay-supported MoS_2 catalyst gave similar high conversions of pyrene, and the product distribution was changed. Much more of the decahydropyrene (three isomers) and hexadecahydropyrene (three isomers) were formed, owing to the increased activity for hydrogenation of the di- and monoaromatic intermediates. The products also included those formed by rearrangement and hydrocracking reactions.

The commercial nickel-molybdenum catalyst (HDN-30) gave a lower conversion of pyrene (69%). Yields of the hexadecahydropyrene and decahydropyrene products were considerably lower than those obtained with either the NiSMM or MoS_2 -NiSMM catalysts, but the dihydropyrene component was greater.

A reaction of pyrene with NiSMM was also carried out at 400°C. As expected, the conversion was lower because of the lower equilibrium constant at the higher temperature. The yields of the hexadecahydropyrene and decahydropyrene were low, but somewhat more cracking occurred.

Heteroatom Removal from Model Compounds. The hydrodeoxygenation, hydrosulfurization, and hydrodenitrification activities of NiSMM were investigated by using *p*-cresol, dibenzothiophene, and quinoline as test substrates. The reactions were carried out at 400°C for 3 hours in the presence of 1000 psi of molecular hydrogen. Relevant analytical data are given in Table 1.

The reaction of *p*-cresol with NiSMM gave a high conversion (83%) of the substrate into many hundreds of products. Some of the major components are reported in Table 1. The reaction of *p*-cresol gave considerable amounts of *o*- and *m*-cresols, which could have been formed by acid-catalyzed rearrangement reactions. Toluene and methylcyclohexane were also major products. The reaction of dibenzothiophene also gave hundreds of products, including methylcyclopentane, benzene, toluene, ethylbenzene, and biphenyl as the major products. Quinoline gave tetrahydroquinoline, alkylbenzenes, aniline, and methylpyridine as the major products.

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TABLE I
Hydrocracking and Hydrogenation Activity of Synthetic Clays
Reaction Time = 3 h, H_2 = 1000 psi
Catalyst wt/Substrate wt = 0.5

Catalyst	Temperature, °C	Substrate, mmol	Conv., %	Major Products, mmol
SMM	350	BB (2.71)	2	Benzene (0.03) Toluene (0.03) Ethylbenzene (0.01)
NiSMM	350	BB (2.72)	67	Benzene (1.46) Toluene (0.11) Ethylbenzene (0.41)
Reduced NiSMM	350	BB (2.79)	65	Benzene (1.29) Toluene (0.13) Ethylbenzene (0.45)
Sulfided- NiSMM	350	BB (2.75)	82	Benzene (1.84) Toluene (0.02) Ethylbenzene (0.65)
Sulfided- MoSMM	350	BB (2.89)	34	Benzene (0.05) Toluene (0.05) Ethylbenzene (0.05) Cyclohexane (0.08)
Sulfided- MoNiSMM	350	BB (2.80)	92	Benzene (1.18) Toluene (0.10) Ethylbenzene (0.40) 4,5-Dihydronaphthalene (0.21) Methylcyclohexane (0.14) Ethylcyclohexane (0.10) Tetralin (0.15)
Sulfided- NiSMM	350	Pyrene (2.43)	90	Hexadecahydronaphthalene (0.07) (3 isomers) Decahydronaphthalene (0.36) (3 isomers) 1,2,3,3a,4,5-Hexahydronaphthalene (0.26) 1,2,3,6,7,8-Hexahydronaphthalene (0.38) 4,5,9,10-Tetrahydronaphthalene (0.06)
Sulfided- HDN-30 Ni-Moly	350	Pyrene (2.47)	69	Hexadecahydronaphthalene (0.03) (3 isomers) Decahydronaphthalene (0.12) (3 isomers) 1,2,3,3a,4,5-Hexahydronaphthalene (0.21) 1,2,3,6,7,8-Hexahydronaphthalene (0.45) 4,5,9,10-Tetrahydronaphthalene (0.24) 4,5-Dihydronaphthalene (0.64)
Sulfided- NiSMM	400	Pyrene (2.66)	65	Hexadecahydronaphthalene (trace) Decahydronaphthalene (0.05) (3 isomers) 1,2,3,3a,4,5-Hexahydronaphthalene (0.13) 1,2,3,6,7,8-Hexahydronaphthalene (0.17) 4,5,9,10-Tetrahydronaphthalene (0.06) 4,5-Dihydronaphthalene (0.41)
Sulfided- NiSMM	350	Naph. (3.98)	62	Tetralin (2.18) Benzene (0.04) Toluene (0.02) Indan (0.02)
Sulfided- NiSMM	400	<i>p</i> -Cresol (4.66)	83	Toluene (0.17) Methylcyclohexane (0.16) <i>m</i> -Cresol (0.74) <i>o</i> -Cresol (1.90)
Sulfided- NiSMM	400	DBT (2.78)	84	Methylcyclopentane (0.26) Benzene (0.28) Toluene (0.10) Ethylbenzene (0.14) Biphenyl (0.13)
Sulfided- NiSMM	400	Quinoline(4.11)	87	C ₂ -benzene (0.25) Tetrahydroquinoline (0.10) Aniline (0.20) Methylpyridine (0.10)

DBT = Dibenzothiophene.
BB = Bibenzyl.